1955

A study of the structure of titanium diffusion coatings on iron and steel

Pao-Jen Chao

A STUDY OF THE STRUCTURE OF TITANIUM DIFFUSION COATINGS ON IRON AND STEEL

BY

PAO-JEN CHAO

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1955

Approved by - N. J. Grant

Research Professor of Metallurgy

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. M. E. Straumanis, Research Professor in Metallurgy, for his guidance and valuable suggestions concerning this investigation, to Dr. A. W. Schlechten, Professor and Chairman of the Department of Metallurgical Engineering, for his advice and guidance; and to Dr. S. T. Shih, for his helpful suggestions.

The author would also like to express his appreciation for the opportunity of doing this work for the Air Force under Contract No. AF 33(616)-75.

CONTENTS

LIST OF ILLUSTRATIONS

FIGURE PAGE

FIGURE PAGE

INTRODUCTION

A. Diffusion Coating on Metals

It is probably true that every metal will diffuse into every other metal to some extent[1]. According to Dovey, a diffusion coating may be defined as a coating achieved by a cementation process operated by a diffusion mechanism[2]. Technically important diffusion treatments have been successfully applied only to alloy systems having sufficient solubility ranges or compounds, or both; such treatments are: calorizing, carburizing, chromizing, sherardizing, and siliconizing. These various diffusion coatings on metals are used either to resist corrosion and wear, or for decorative purposes.

For metals such as titanium, there has not been any successful industrial method developed yet to electroplate them from aqueous or organic solution, but it is possible to deposit such metals on common metals by a diffusion process. In general, a diffusion coating produces a smaller diamensional change and adheres more strongly to the base metal than an electroplated coating. The physical and chemical properties as well as structural characteristics of diffusion coatings are largely determined by the diffusion mechanism.

---

(1) Rhines, F. N., Diffusion Coatings on Metals, A. S. M. Surface Treatment of Metals, 1941, p. 123.

(2) Dovey, D. M., Jenkins, I., and Randle, K. C., Diffusion Coatings, Properties of Metallic Surfaces, Institute of Metals monograph, No. 13, 1952, pp. 213-236.

B. The Importance of Titanium Diffusion Coatings on Iron and Steel

Titanium, with many desirable physical and chemical properties, has tremendous possibilities as a strategic material. Its excellent corrosion resistance is the most prominent characteristic of value to engineers. However, many production, fabrication, and cost problems remain to be solved before titanium can be seriously considered for commercial uses. It was found during World War II that the usual methods of protecting metals from corrosion were often inapplicable where high corrosion resistance is needed and fine dimensional tolerances must be kept. Many investigations have been undertaken concerning this serious subject. It has been shown that titanium diffusion coatings impart excellent corrosion resistant to other metallic articles, especially for small, intricately shaped pieces.

Iron and steel, as is well known, are the most widely used materials for engineering, but they are readily subject to corrosion. It is obvious, that titanium diffusion coatings can help solve this vital problem.

C. The Problem of the Thesis

A series of experiments have been made in the Metallurgical Engineering Department of the Missouri School of Mines and Metallurgy for the investigation of titanium diffusion coatings. The technique of applying the titanium diffusion coatings on iron and steel is still in the experimental stage. A few of the physical properties and chemical compositions of such coatings have been determined, but the structures have not yet been extensively

studied. As the correlations of the structures and the desirable properties are valuable for improving the quality of titanium diffusion coatings on iron and steel, an investigation was undertaken to explore these structures by metallographic methods.

REVIEW OF PREVIOUS LITERATURE

For the study of the structure of diffusion coatings, a classification of titanium alloying elements as made by Jaffee[3], may be useful:

INTERSTITIAL

THE ALPHA PHASE STABILIZING ELEMENTS:	THE BETA PHASE STABILIZING ELEMENTS:
Oxygen	Hydrogen
Nitrogen	
carbon	

SUBSTITUTIONAL

THE ALPHA PHASE STABILIZING ELEMENTS:	THE BETA PHASE STABILIZING ELEMENTS:	
	Isomorphous Elements:	Eutectoid Elements:
Aluminum	Molybdenum	Manganese
Tin	Vanadium	Iron
	Columbium	Chromium
	Tantalum	Cobalt
		Nickel
		Copper
		Silicon

The beta-eutectoid elements are listed in order of increasing activity of the eutectoid reaction.

The general principles governing the operation of diffusion processes have been studied by Rhines[1]. He found that the struc-

---

(3) Jaffee, R. I., General Physical Metallurgy of Titanium Reviewed, J. of Metals, Feb., 1955, Sec. 1, pp. 247-252.

(1) Rhines, F. N., op. cit. on page 1, pp. 123-124

ture of a diffusion coating is directly related to the constitutional diagram of the corresponding alloy system. The phases in the coating can be predicted by the phase diagram but they sometimes cannot be identified, and occasionally phases not predicted appear. These discrepancies are the result either of incorrect constitutional diagrams or insufficiently delicate experimental technique in the production of examination of the diffusion coatings.

According to Rhines[1], the layers formed in a diffusion coating correspond in order of occurrence to single phase regions in binary diagrams; interfaces correspond with two phase regions, but in ternary systems layers can correspond to both one and the two-phase regions. A more general statement which applies to systems of all degrees of complexity is: the layers formed by the isothermal and isobaric diffusion of metals across an interface correspond in kind and in the order of their occurrence to all regions in the phase diagram lying between the concentration of the original bodies and having three or more degrees of freedom according to the phase rule (two or more degrees of freedom in the conventional temperature-concentration section where pressure is disregarded).

Surface treatments cannot always be carried out at a constant temperature and pressure, and often other external factors resulting from the mechanics of individual processes interfere with the normal course of diffusion whereby certain deviations from this principle arise.

The constitutional diagrams of the titanium alloy systems which would be necessary for the present study have not yet been completed. Comstock, Urban, and Cohen[4] have presented a phase diagram of iron rich alloys of the iron-titanium system, and Worner[5] presented a study of titanium rich alloys of the same system.

Hadley and Derge[6] worked out the ternary phase diagram of the iron-oxygen-titanium alloy system. Hawkes[7] published isothermal sections at 700°C., 800°C., and 1100°C. of the ternary phase diagram of the iron rich corner of titanium-carbon-iron system. The information of other ternary systems of titanium and other elements are not available.

For better identification of phases in titanium alloys, Ence and Margolin[8] developed a new etching technique, the so called cumulative electrolytic stain-etching method. The use of stain

---

(4) Comstock, G. F., Urban, S. F., and Cohen, M., Titanium in Steel, Pitman Publishing Corporation, 1949, p. 48.

(5) Worner, H. W., The Constitution of Titanium Rich Alloys of Iron and Titanium, J. of the Inst. of Metals, Vol. 79, May 1951, pp. 173-188.

(6) Hadley, R. L., and Derge, G., Equilibrium Between Titanium in Liquid Iron and Titanium Oxides, J. of Metals, Vol. 7, June 1955, Sec. 1, pp. 55-60.

(7) Hawkes, M. F., Constitutional Diagram of Carbon-Iron-Titanium, Metals Handbook, American Society of Metals, 1948, p. 1225.

(8) Ence, E., and Margolin, M., Phases in Titanium Alloys Identified by Cumulative Etching, J. of Metals, Vol. 6, No. 3, March 1954, pp. 346-348.

etching for phase identification is based on the differential rate of oxidation of the microconstituents. When electrolytically etched, the various phases in titanium alloys appear in different tints. Under the microscope carbides are yellow or orange-yellow, while alpha and transformed or retained beta titanium appear violet or blue; TiMn appears bluish green; ϵ phase of titanium-manganese system is violet or black; the phase, TiFe, appears bluish green; β-titanium is usually purplish red or orange.

EXPERIMENTAL PART

A. Apparatus and Equipment

The apparatus and equipment used in this investigation were as follows:

1. Electrolytic polishing cell--Used for polishing titanium metal. Included in this cell are a glass tank, a thermometer, the electrolyte, a cathode made of Remington Arms cold rolled titanium plate, an anode which is the specimen to be electro-polished, and a glass stirrer. The arrangement of the cell is shown in Figure 1.
2. Electric circuit for the electrolytic polishing cell--The power drawn from an A. C. source passed first through a V-5M Variac transformer which reduced the voltage, then through a 1000 milliampere selenium rectifier which converted the current from A. C. to D. C. A 1.2 amp., a 355 ohm rheostat and switch, a 150 milliampere D. C. ammeter, and a150 volt voltmeter completed the arrangement. This hook-up is shown diagrammatically in Figure 2.
3. Electrolytic stain-etching cell--This cell was used for cumulative stain-etching. Included in this cell are a glass tank, a stainless steel base plate, a bakelite mask, the electrolyte, a pair of stainless steel forceps, and the specimen to be etched. This cell is sketched in Figure 3.
4. The electric circuit for the electrolytic stain-etching cell was the same as that for the electrolytic polishing cell.

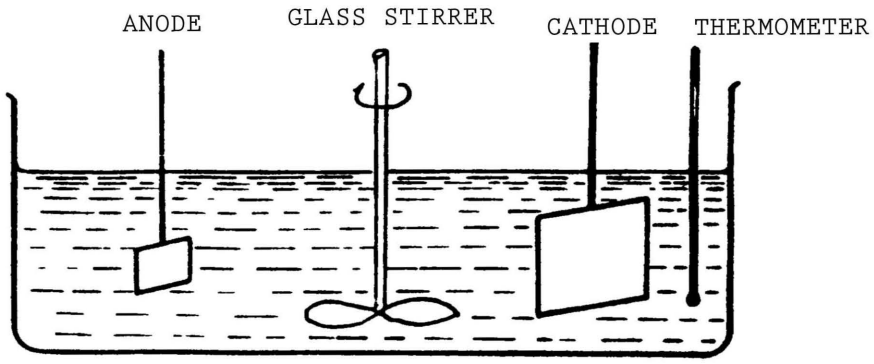


Figure 1. The Arrangement of Electrolytic Polishing Cell.

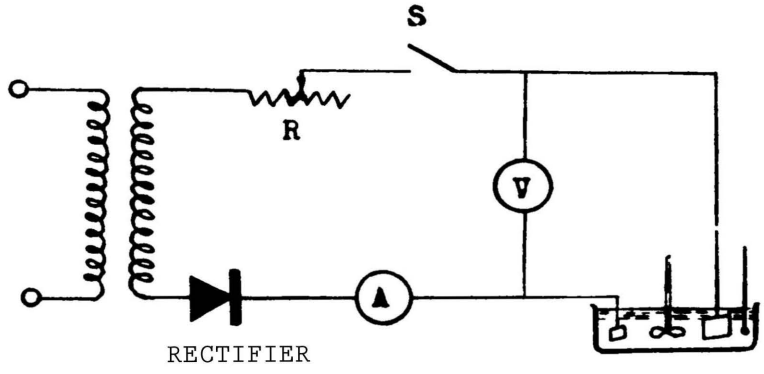


Figure 2. The Electric Arrangement for The Electrclytic Polishing Cell.

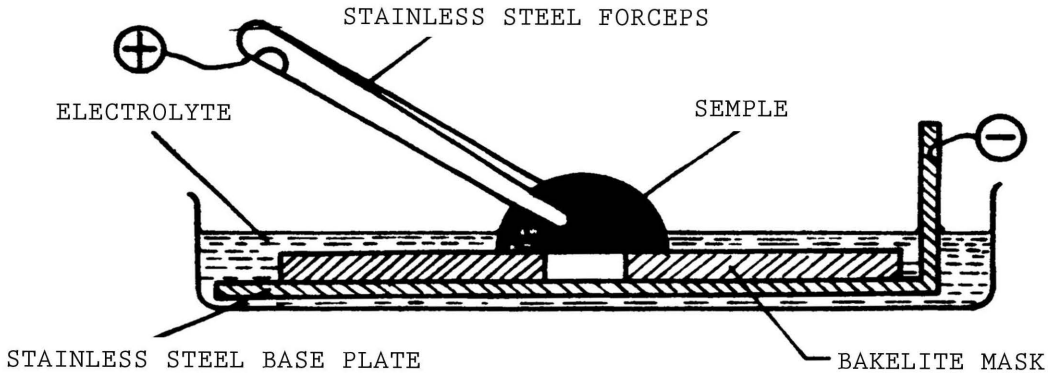


Figure 3. The Arrangement of Electrolytic stain-etching Cell.

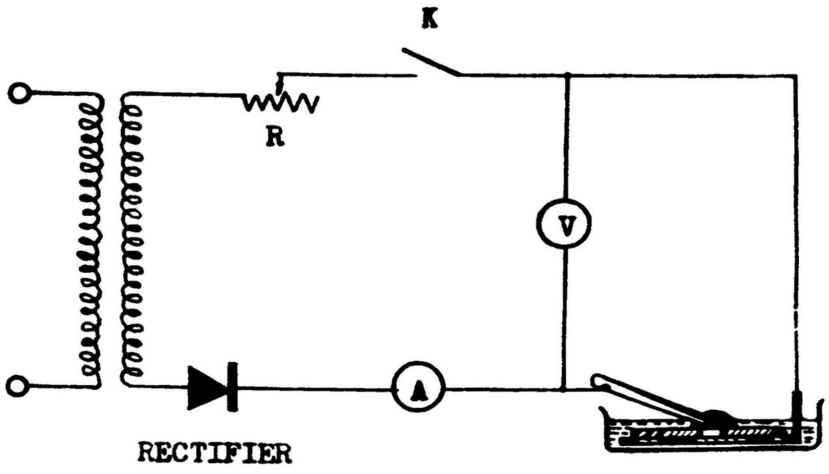


Figure 4. The Electric Arrangement for Electrolytic Stain-etching Cell.

5. Buehler mounting press, used to mount specimens to be examined.
6. Behr-Manning belt grinder, used to grind samples. Grinders were provided with No. 120 and No. 320 belts respectively.
7. Buehler multi-speed polishing wheels, covered with canvas, billiard table covering, wool broadcloth and velveteen respectively, used for polishing samples.
8. Metallurgical microscope with calibrated screw micrometer eyepiece, used for examination and measurement of the thicknesses of coating and diffusion zone.
9. Bausch and Lomb Research Metallograph, for metallographic examination of samples.

B. Material and Reagents

1. Remington Arms cold rolled titanium plate.
2. Cold rolled, annealed, commercial pure titanium plate produced by Titanium Metals Corporation of America.
3. Iodide titanium furnished by Foote Mineral Company, Philadelphia, Pa.
4. Armco ingot iron plate and billet.
5. 1/0 to 4/0 Fisher metallographic emery paper.
6. 400 and 600-mesh carborundum powder.
7. Levigated magnesium oxide powder.
8. 2μ, 6 to 10μ, and 30μ Dymo diamond compounds made by Elgin National Watch Company.
9. Squibb mineral oil.

10. Electrolyte for electrolytic polishing, consisting of:

Glacial acetic acid	1000 ml
Perchloric acid (sp. gr. 1.54)	60 ml

11. Etchant for titanium metal and its alloys of the composition:

HF	1 ml
HNO_3	12 ml
H_2O	87 ml

12. Electrolyte for cumulative electrolytic stain etching of the composition:

Oxalic acid	5 gm
Citric acid	5 gm
Orthophosphoric acid (85 pct.)	5 ml
Lactic acid (85 pct.)	10 ml
Ethanol (95 pct.)	60 ml
Water	35 ml

C. Experimental Procedure

1. Polishing of titanium metal and titanium coatings on ingot iron.

The sample of cold rolled, annealed, Remington Arms titanium plate was prepared by grinding on emery paper to 3/0 grade, before electrolytic polishing. Then the sample which was the anode was suspended vertically in the electrolyte for polishing (Figure 1), about 3 cm. from the cathode, which was made of the same titanium plate having an area greater than that of the anode. The current was allowed to flow for about 2 minutes. A current density of 30 to 40

amperes per square decimeter was applied. The electrolyte was stirred by a glass stirrer driven by a motor and the temperature of the electrolyte was kept below 4.4°C. (40°F.).

However, as the electropolished samples prepared in this way did not show any special advantage over the mechanically polished ones, all of the other samples used in this research were simply prepared by mechanical polishing. So, samples made of cold rolled, annealed commercially pure titanium plate, of iodide titanium and of titanium-oxygen alloy coatings on ingot iron were polished by mechanical means. These samples were polished on emery papers down to 3/0 grade, then polished successively on lapping wheels covered with canvas, billiard table covering, and velveteen respectively. 400 and 600-mesh carborundum powders were used as abrasives on the wheels covered with canvas, while levigated magnesium oxide was used for the wheels covered with billiard table covering and velveteen. The samples polished by the aforementioned method, were almost scratch free.

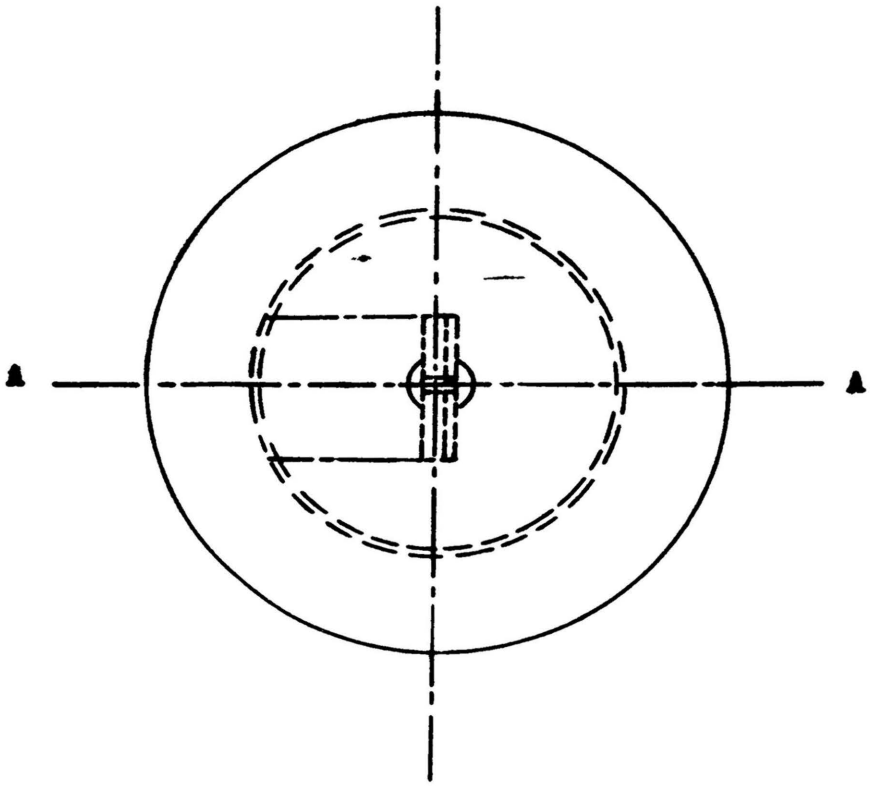
2. Mounting and polishing of cross sections of titanium alloy coatings on ingot iron and plain carbon steels.

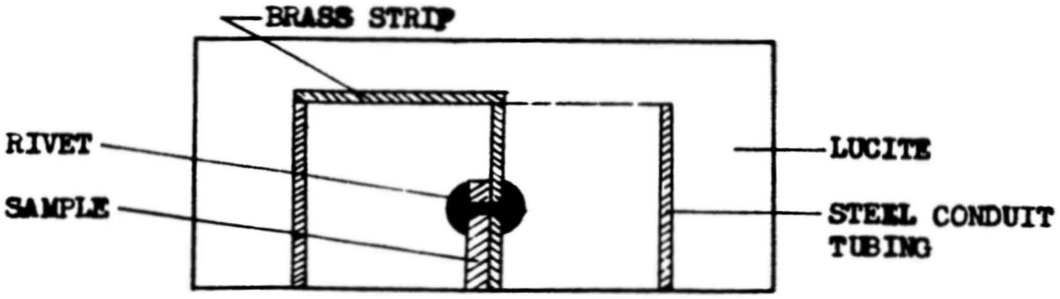
Samples with various types of titanium alloy coatings were cut with a hack saw from large plated objects. They were ground on belt grinders to remove the rough edges which resulted from cutting. A hole of about 2 mm. diameter was drilled near one edge of each sample. Then the sample was attached to a brass strip with an aluminum rivet to help the

sample stand perpendicularly. Then the sample was placed in the middle of a short piece of steel conduit tubing of 3/4 inch in diameter as shown in Figure 5. Finally the whole sample was embedded in hard crystal lucite in a Buehler mounting ress. The mould temperature was 130°C., and a pressure of 3000 pounds per square inch was applied. The mold was then allowed to cool and the sample was taken out after it was below 80°C. The mounted specimen was then ground on the Behr-Manning belt grinders, followed by successive polishing on emery paper down to 3/0 grade and polished on wheels as used for polishing titanium metal. To avoid excessive rounding of the edge, the samples were finally polished on wheels covered with wool broadcloth on which, Squibb mineral oil was sprayed as a lubricant, and Elgin Dymo diamond compounds were used.

3. Etching techniques.

The well polished samples of various kinds of titanium metal and the titanium alloy coatings on ingot iron and plain carbon steels were etched with a solution containing 1 milliliter of hydrofluoric acid, 12 milliliters of nitric acid and 87 milliliters of water. Other etching solutions of different composition were also tried, but the one just mentioned gave the best result. However, it was still not completely satisfactory as it tended to etch certain phases preferentially and caused severe pitting, particularly in fine grained specimens. The etching rate was found to vary with the various phases. Continuous agitation of the sample in the etching solution was





SECTION A-A

SCALE: 3:1

Figure 5. The Arrangement for Mounting of Sample.

necessary to prevent pitting or grooving. By etching some scratches were removed and the microstructure was revealed.

For cumulative electrolytic stain etching, each of the pre-etched samples was placed as shown in Figure 3, and the circuit was closed by the contact switch. Since the specimen was rapidly heated and interfering gas bubbles were formed, the time for one etching cycle had to be limited to a fraction of a second. To obtain a properly etched sample, the circuit was opened and closed 5 to 10 times. Current densities were determined by the thickness of the bakelite mask (2 to 6 mm. were used), and the size of the opening in the mask (9.42 and 18.84 sq. mm. were used). Voltages in the range of 20 to 100 volts were most frequently used and for best differentiation of phases, 50 to 90 volts were applied.

With cumulative stain etching, the surfaces of the coatings and of the titanium metal, and the cross sections of the samples showed the coating as well as diffusion in different colors. At first, the surface of the sample appeared yellow, and then with additional etching the color changed to brown, orange.red, rosy red, violet, and blue. With further increase in etching time the color cycle repeated with some modification. Generally the best distinction between phases occurred when the blue color appeared for the second time. The etching time for the appearance of the blue color varied with the composition and type of alloying constituents. The uncoated area on the surface of ingot iron and steel samples

and the core of the base metal of the sectioned samples was slightly darkened after stain etching, but changed to a white color after repeated stain etching.

To etch the polished sample with the solution consisting of 1 milliliter hydrofluoric acid, 12 milliliter nitric acid and 87 milliliter water prior to stain-etching is not necessary, but was done to give a sharper outline of constituents and to improve the general appearance of the microstructure. When pre-etching was not done, the colors obtained were consistent, but were different from those developed after pre-etching.

4. Examination of the structure of titanium metal and of titanium diffusion coatings.

The samples prepared by the procedures described were examined and photographed on a Bausch and Lomb Research Metallographic microscope. For better record and presentation color photomicrographs were made using Kodak Ektachrome Type B films, to show the different phases in titanium metal, titanium coatings, and diffusion layers.

The thickness of coatings and of the diffusion layer were measured on a simple Bausch and Lomb metallurgical microscope with a calibrated screw micrometer eyepiece. Several spots were measured on each sample, and the average thickness was taken.

D. Data

1. The Struc ure of Titanium Metal

The microstructure of samples of cold rolled annealed titanium plates produced by Remington Arms and by Titanium Metals Corporation of America, and of iodide titanium were revealed after etching with the previously mentioned etchant (HF : HNO_3 : H_2O = 1 : 12 :87 by volume). In the sample of Remington Arms titanium, many spots were found. After strain etching, these spots had a pink color (Figure o). There were no such spots found in the other two samples. The structure of the titanium plate made by Titanium Metals Corporation of America is shown in Figure 7. It had a different grain shape as compared with Remington Arms titanium and the grain bcundaries of this sample were tan in color after stain etching. The iodide titanium showed a structure different from the others, the grain shape was nearly rhombic as shcwn in Figure 8. The grain boundaries of this sample were a rosy red after stain etching. It was also found that the blue color developed on each sample was different, being blue on the iodide titanium, bluish green on the Titanium Metal Corporation titanium, and light blue on the Remington Arms titanium.

2. The structure of titanium coatings on ingot iron and plain carbon steels made by the titanium-oxygen alloy method.

Eighteen samples of ingot iron were coated under different conditions in fused salt baths using titanium oxygen alloy as described by Shih and Straumanis[9]. The thicknesses of coatings

---

(9) Shih, S. T., and Straumanis, M. E., Progress Report No. 12, July, 1954, Electrodeposition of Titanium Project, Contract No. AF33(616)-75, U. S. A. F.

TABLE I

Variation of Thickness of Titanium Coating and Diffusion Layer on Ingot Iron With Temperature, Time, and Bath Composition, as Measured Under the Microscope.

Sample No.	Coating Temp.	Coating Time	Bath Composition	Thickness of Coating Layer (mm)	Thick ess of Diffusion Layer (mm)
1	850	4	90% KCl, 10% $Ti_{95}0_5$	0.0040	No diffusion layer.
2	850	6	90% KCl, 10% $Ti_{95}0_5$	0.0060	No diffusion layer.
3	950	2	90% KCl, 10% $Ti_{95}0_5$	0.0080	0.0440
4	950	4	90% KCl, 10% $Ti_{95}0_5$	0.0120	0.0680
5	950	6	90% KCl, 10% $Ti_{95}0_5$	0.0140	0.0880
6	1000	2	90% KCl, 10% $Ti_{95}0_5$	0.0152	0.0820
7	1000	4	90% KCl, 10% $Ti_{95}0_5$	0.0155	0.1352
7a	1000	4	90% KCl, 10% $Ti_{95}0_5$	0.0160	0.1121
8	1000	4	80% KCl, 20% $Ti_{95}0_5$	0.0116	0.0780
9	1000	4	95% KCl, 5% $Ti_{95}0_5$	0.0160	0.0640
10	1000	4	90% NaCl, 10% $Ti_{95}0_5$	0.0150	0.1148
11	1000	4	90% KCl, 10% $Ti_{95}0_5$	0.0120	0.0844
12	1000	4	90% KCl, 10% $Ti_{95}0_5$	0.0120	0.1004
13	1000	4	90% KCl, 10% TiCyclone fines	0.0140	0.0672
14	1000	6	90% KCl, 10% TiCyclone fines	0.0152	0.1028
15a	1000	6	90%KCl, 10% $Ti_{95}0_5$	0.0200	0.1500
15	1000	6	90% KCl, 10% $Ti_{95}0_5$	0.0160	0.1600
16	1000	9	90% KCl, 10% $Ti_{95}0_5$	0.0132	0.1640
17	1150	4	90% NaCl, 10% TiCyclone fines	0.0208	0.2450

and diffusion layers were found to vary with coating conditions and are tabulated as shown in Table 1. The structure of the coating made at 1000° C. for 3 hours in a bath consisting of 85 percent potassium chloride and 15 percent titanium-oxygen alloy containing 5 atomic percent oxygen is shown in Figure 9. It was found that the color developed by stain etching and the grain shape of this sample were quite different from those of the various titanium metal samples. Its grain shape was similar to a hexagon, and the grain boundaries appeared light yellowish green in color. In each grain from the grain boundary inward, there were two successive zones, the first one was aquamarine and the second was rosy red. The remaining area within each grain had a bluish green color mottled with yellow and yellowish green spots.

The cross section of a sample coated at 1000° C. for 6 hours in a bath consisting of 90 percent potassium chloride and 10 percent titanium fines is shown in Figure 10. In this sample, the coating consists of four layers, and many gaps exist between the coating and the diffusion layer. After stain etching, these four layers in the coating showed various blue colors. The first layer from the top was aquamarine, the second was bluish purple, the third was yellowish green, and the fourth was light aquamarine. There were a few scarlet spots in the first two layers, and the other two layers were porous. The diffusion zone appeared as a blend of violet, tan, gree, red, and yellow tints; it was composed of columnar crystals with their long axes lying parallel to the direction of growth. (See Figures 11 and 12 respectively).

The cross section of a coating on ingot iron made at 1050°C. for 3 hours in a bath consisting of 90 percent potassium chloride and 10 percent powdered titanium fines with addition of a small amount (about 1 percent) of silicon is shown in Figure 13. The coating was porous, and the grain boundaries in the diffusion layer were widened, but the grain size of the core was small. The cross section of another sample coated under the same conditions except that no silicon was added to the bath is shown in Figure 14. It can be seen that the grain boundaries in Figure 14 are much wider than those shown in Figure 13. After stain etching, both coatings appeared in light blue color.

Figure 15 shows the cross section of a titanium coating on 0.36 percent carbon steel coated by heating at 1050°C. for 3 hours in a bath containing 90 percent potassium chloride and 10 percent titanium fines. The coating was very thin only 0.004 mm and no diffusion layer could be detected. Figure 16 shows the cross section of a coating on the same steel made at similar conditions except that a small amount of silicon powder was added to the bath. The coating of this sample was 0.007 mm, almost twice as thick as that shown in Figure 15. Also a yellow band appeared between the coating and the core after stain etching.

Figure 17, shows that cross section of a sample of 0.45 percent carbon steel coated with titanium at 1100°C. for 4 hours in a bath consisting of 90 percent potassium chloride and 10 percent titanium-oxygen alloy containing 5 atomic percent oxygen, with addition of silicon in a small amount. The coating of this sample on the average was thick (0.0065 mm.)

and no diffusion layer was found. Figure 18 shows the cross section of another sample made under the same conditions except that no silicon was added to the bath. This sample had a thinner coating, (0.003 mm.) which peeled off easily; after stain etching, both coatings showed the same bluish green color.

A set of two samples of 0.36 percent carbon steel were coated at 1100°C. for 3 hours in a bath consisting of 9 grams of potassium chloride and 1 gram of titanium fines with and without the addition of a very small amount of fine zirconium powder respectively. Figure 19 shows the cross section of the sample coated in the bath with zirconium. The coating was 0.0150 mm. thick and adhered to the base metal very well. The coating of this sample obtained without the addition of zirconium to the bath was 0.0055 mm. thick. (Figure 20)

2. The structure of titanium coatings on carbon steels made in fused salt bath with metallic titanium powder.

The samples of carbon steels were coated by R. P. Abendroth[10] in the following manner: the steel specimens were placed in porcelain crucibles which were then filled with titanium powder. The titanium powder was agitated to insure a uniform distribution, so that the sample was surrounded on all sides by at least a quarter of an inch of titanium powder. The crucibles were next filled with sodium chloride and heated at 950°C. for 6 hours in

---

(10) Abendroth, R. P., Effect of Carbon Content In Steels Upon The Deposition of Titanium From A Fused Salt Bath, M. S. Thesis in Metallurgy, Missouri School of Mines and Metallurgy, 1954, pp. 9-10.

in a Glo-bar type furnace. The section of 0.12 percent carbon steel sample is shown in Figure 21. There were many voids found between the coating and the diffusion zone in this sample. After stain etching, the coating appeared in two colors, the outer part was blue, the inner part was orange red, and the part in between showed a blend of these two colors.

Figure 22 shows the cross section of a coated 0.15 percent carbon steel sample. After ordinary etching, a thin and even coating was revealed, and a diffusion layer could be seen but without a sharp boundary between this layer and the inner core. After stain etching, the coating appeared light blue in color and the diffusion zone appeared as a bright yellow band.

The coating on the 0.36 percent carbon steel sample was very thin (0.0030 mm.) and peeled off easily. No diffusion layer could be found. (Figure 23) Another sample of the same steel was coated by using titanium powder and a mixture consisting of 20 percent vanadium oxydichloride ($VOCl_2$) and 80 percent sodium chloride. It was found that this sample had a thicker coating (0.0062 mm.) than the one coated without the addition of $VOCl_2$, and a diffusion layer without sharp boundary between itself and the core appeared after stain etching, (Figure 24) both appearing bright yellow in color, but the brightness decreased gradually inward from the outer edge of the coating to the inner core.

For a study of the effects of decarburization on the mechanism of coating, a set of four samples of 0.36 percent carbon

steel were decarburized by Abendroth at 950°C. for 1, 2, 3, 3/4, and 4 1/2 hours respectively. The loosely adhering oxide scale was allowed to remain, and the samples were then plated at 950°C. for 8 hours, by the afore mentioned method(10).

The titanium deposited on the oxide scale to a considerable thickness (0.1200 mm.); and after stain etching the coating showed a normal blue color similar to pure titanium metal (Figure 25). The coating seemed to be a single phase, but could be easily peeled off.

Another set of samples of 0.36 percent carbon steel were decarburized and coated under the same conditions as the former one, except that the oxide scale was completely removed before being subjected to coating. It was found that the coatings were very thin (0.0700 mm.) and did not adhere to the base metal very well. The blue colors developed by stain etching were lighter on these coatings than on those with adhering oxide scale.

4. The Structure of Titanium Coatings on Ingot Iron Obtained by the Iodide Titanizing Method.

A titanium coating on ingot iron was made by embedding the iron in a mixture consisting of 10 grams of iodine and 40 grams of titanium fines and heating the whole at 1000°C. for 4 hours in a Glo-bar type furnace. A cross section of this

---

(10) Abendroth, R. P., Ibid.

sample is shown in Figure 26. The coating layer showing many cracks and the diffusion zone were thick, and between them there were many voids. After stain etching, the outer part of the coating appeared blue in color and the inner part reddish violet.

A set of two samples were made by embedding the ingot iron in a mixture consisting of 120 grams alumina, 120 grams titanium powder (+65 mesh), and 30 grams of iodine which then were heated at 1100°C. for 4 hours. The structure of one of the samples is shown in Figure 27. This coating was thin (0.0129 mm.) and uneven. After stain etching it showed a bright white color. Another sample was put in a stainless steel wire cage which was then embedded in the same mixture and heated. It was found that the coating was fairly thick (0.260 mm.) and even but somewhat porous. (Figure 28). The grain boundaries in the diffusion zone of the latter sample were wider than those of the former one. It was also found that under the coating there were voids situated in the diffusion zone. After stain etching, the coating showed a yellowish green color.

5. The Structure of Titanium Coatings Obtained in Presence of Ammonium Chloride.

Coatings on ingot iron and 0.15 percent carbon steel were prepared by surrounding each sample by a stainless steel wire cage, which was then embedded in a mixture consisting of 120 grams alumina, 120 grams titanium powder (+65 mesh), and 45 grams ammonium chloride, and was heated at 1100°C. for 4 hours. The coating on ingot iron (Figure 29) was very thick (0.0133 mm.) and had a conglomerate structure. Its diffusion layer had a similar appearance to that of the sample show in Figure 27.

The coating on 0.15 percent carbon steel was 0.0101 mm. thick, (Figure 30), and had a coarse grained structure adhering very well to the base metal, but no diffusion layer was found in this sample. After stain etching, the coatings of both samples change in color from their orginal golden yellow to a reddish purple.

6. The Structure of Titanium Coating on Ingot Iron Deposited in the Titanium Lower Chloride Bath.

This coating was prepared by the method described by Shis and Straumanis[11]. It was coated at 1100°C. for 4 hours (Figure 31) on ingot iron. The coating was thin, (0.0020 mm.) porous, and uneven, and showed a light blue color after stain etching. A thick diffusion zone (0.0520 mm.) was found in this sample.

7. The Structure of Titanium Coating Obtained in the Presence of Hydrogen Chloride Gas.

A titanium coating on ingot iron was made by passing dry hydrogen chloride gas through titanium powder heated (at 1100°C. for 3 hours), in which an iron specimen was embedded. The cross section of such a prepared sample is shown in Figures 32 and 33. The coating showed a blue color after stain etching. The grain boundaries of the columnar structure in the diffusion zone were wide and shiny. There were many cavities in the diffusion layer. It was found that the coating adhered to the base metal very well.

---

(11) Shih, S. T., and Straumanis, M.E., Progress Report No. 11, Dec. 1954, Electrodeposition of Titanium Project, Contract No. AF33(616)-75, U. S. A. F.

Fig. 6. The structure of cold rolled, annealed Remington Arms titanium plate. 250x.
After stain-etching, grains showed a light blue color, the spots a pink color.

Fig. 7. The structure of cold rolled, annealed commercial pure titanium plate produced by Titanium Metals Corporation of America. 250x.
After stain-etching, the majority of the grains originally showed bluish green color under the microscope.

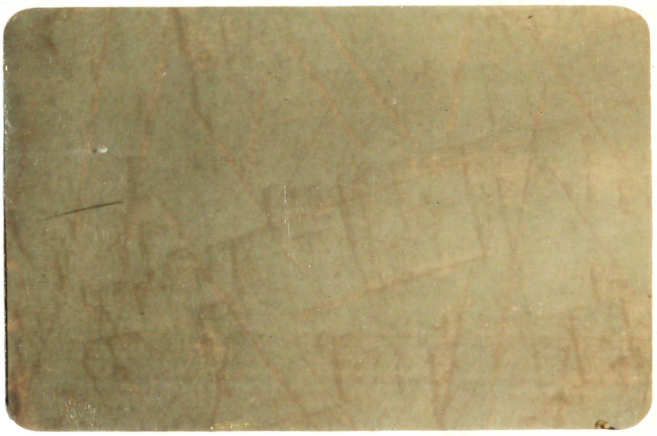


Fig. 8. The structure of iodide titanium produced by Foote Mineral Company. 200x.
After stain-etching the grains originally showed a normal blue color, the grain boundary rosy red.

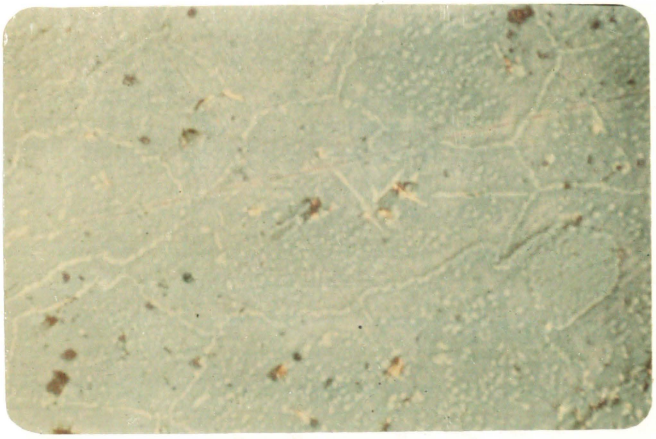


Fig. 9. The structure of titanium coating on ingot iron coated in a fused salt bath containing titanium-oxygen alloy. 200x.
Coating Conditions:
Temperature: 1000°C. Time: 3 hours
Bath composition: 85% KCl, 15% Ti_9O_5
Furnace Atmosphere: He
After stain-etching, the appearance of surface was bluish green.

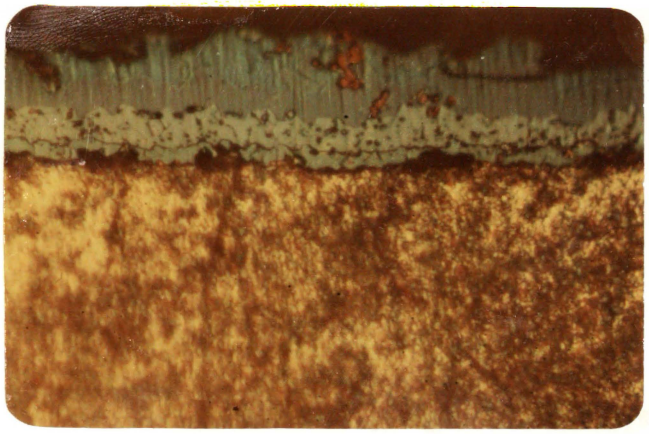


Fig. 10. The cross section of a titanium coating on ingot iron, after stain etching. 520x. The coating appears in the upper part of the Figure.
Coating Conditions:
Temperature: 1000°C. Time: 6 hours
Bath composition: 90% KCl, 10% titanium fines
Furnace Atmosphere: He

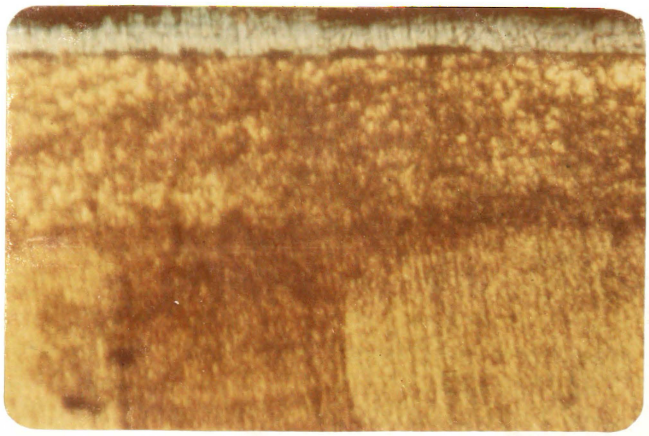


Fig. 11. The colors of the diffusion layer in the same sample as shown in Figure 10 after stain-etching. 200x. The diffusion layer (the upper central part of the figure) showed a blend of violet, tan, green, red, and yellow tints. The line in the middle of this figure is the boundary between the diffusion layer and base metal core.

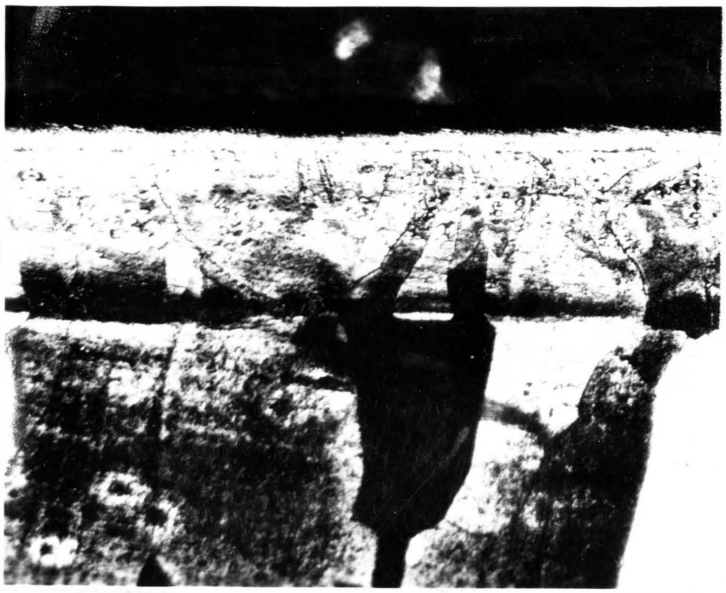


Fig. 12. The structure of the diffusion layer of the same sample as shown in Figure 10. 200x.
Composition of Etchant: HF 1 ml, HNo_3 12ml, and H_2O 87 ml.
The columnar structure of the diffusion layer appears as a band in the upper portion of the photograph.

Fig. 13. The structure of a titanium coating and diffusion layer of an ingot iron sample coated in a fused salt bath with the addition of silicon powder after stain-etching. 150x.
Coating Conditions:
Temperature: 1050°C Time: 3 hours
Bath composition: 89% KCl, 10% Ti fines, and about 1% Si.
Furnace atmosphere: He
The coating appears as a white line in the top portion of the photograph, next to the coating is the diffusion layer, below which is the core of base metal.

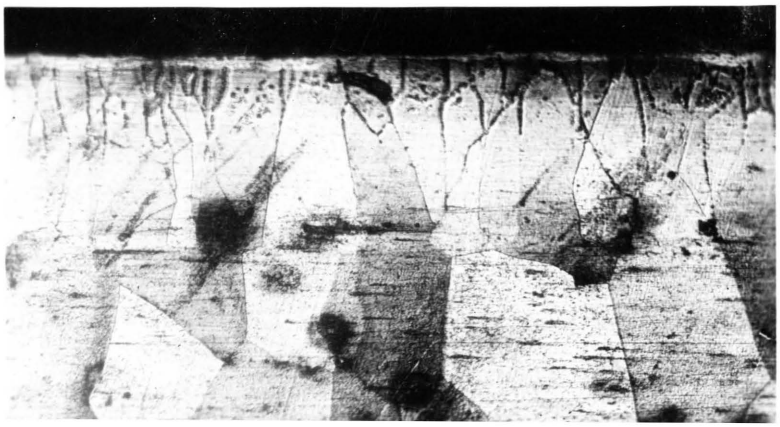


Fig. 14. The structure of a titanium coating and diffusion layer of an ingot iron sample coated under similar conditions as those used for the sample shown in Figure 13, except no silicon in the bath. 150x.

Fig. 15. The cross section of a titanium coating on 0.36% C steel. 100x.
Coating Conditions:
Temperature: 1050°C. Time: 3 hours
Bath composition: 90% KCl, 10% Ti fines
Furnace atmosphere: He
The coating appears as a fine white line in the upper portion of the photograph. Thickness coating=0.0040mm.

Fig. 16. The cross section of a titanium coating on 0.36% C steel coated under similar conditions as those used for the sample shown in Figure 15, but with a small amount of silicon added to bath. 100x. Thickness of coating = 0.007 mm.

Fig. 17. The cross section of a titanium coating on 0.45% C steel. 150x.
Coating Conditions:
Temperature: 1100°C. Time: 4 hours
Bath composition: 89% KCl, 9% Ti_9O_5. and 1% Si
Furnace atmosphere: He
The coating appears as a fine white line in the upper portion of this photograph.
Thickness of coating = 0.0065 mm.

Fig. 18. The cross section of a titanium coating on 0.45% C steel coated under similar conditions as those used for the sample shown in Figure 17, except without silicon in the bath. 150x.
Thickness of coating = 0.003 mm.

Fig. 19. The cross section of a titanium coating on 0.36% C steel. 200x.
Coating Conditions:
Temperature: 1100°C. Time: 3 hours
Bath composition: 9 gm KCl, 1 gm Ti fines, and a small amount of fine Zr powder.
Furnace atmosphere: He
Thickness of coating = 0.0150 mm.

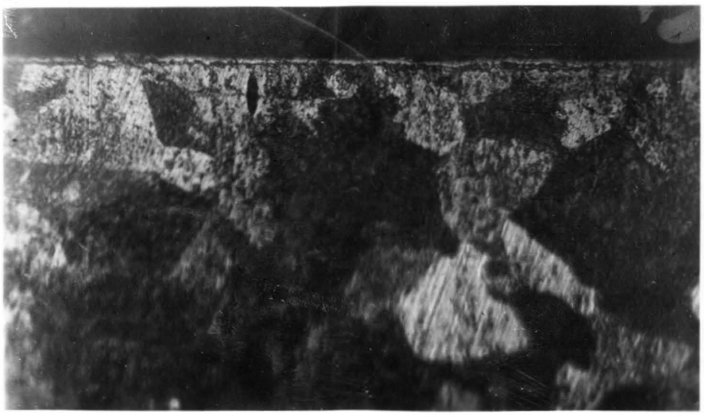


Fig. 20. The cross section of a titanium coating on 0.36% C steel coated under similar conditions as those used for the sample shown in Figure 19, but with no Zr in the bath. 250x.
Thickness of coating = 0.0055 mm.

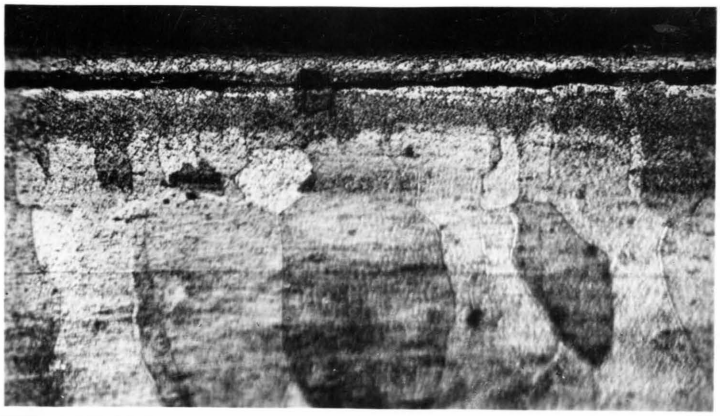


Fig. 21. The cross section of a titanium coating on 0.12% C steel. 250x.
Coating Conditions:
Temperature: 950°C Time: 6 hours
Bath composition: NaCl and Metallic titanium powder
Furnace atmosphere: Air
Thickness of Coating = 0.0120 mm.

Fig. 22. The cross section of a titanium coating on 0.15% C steel. 250x.
Coating Conditions:
Temperature: 950°C Time: 6 hours
Bath composition: NaCl and Metallic titanium powder
Furnace atmosphere: Air
Thickness of Coatings = 0.0045 mm.

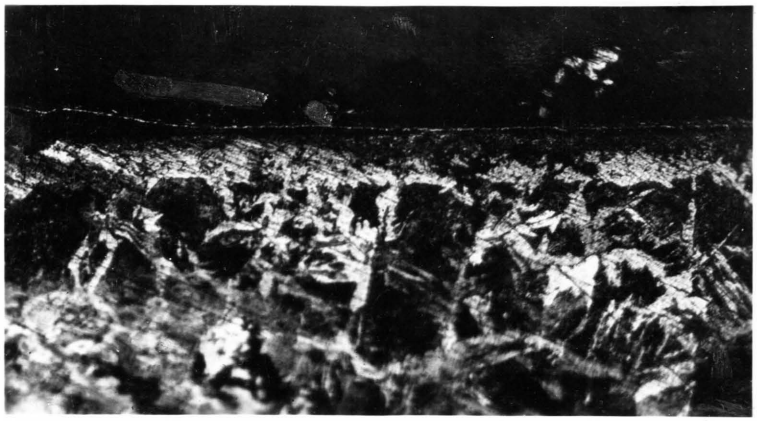


Fig. 23. The cross section of a titanium coating on 0.36% C steel. 250x.
Coating Conditions:
Temperature: 950°C. Time: 6 hours
Bath compositions: NaCl and metallic titanium powder
Furnace atmosphere: Air
The white line in the upper portion of the photograph is the coating. The inclined part of the line is the coating peeling off. Thickness of coating=0.0030 mm.

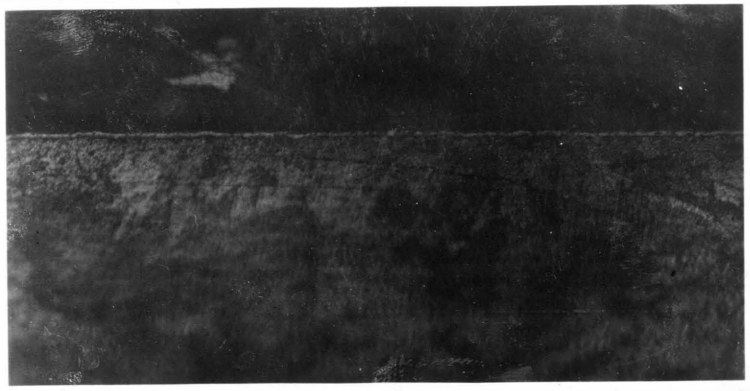


Fig. 24. The cross section of a titanium coating on 0.36% C steel. 250x
Coating Conditions:
Temperature: 950°C Time: 6 hours
Bath compositions: Metallic titanium powder with a salt mixture consisting of 80% NaCl, and 20% $VOCl_2$
Furnace atmosphere: Air
Thickness of Coating = 0.0002 mm.

Fig. 25. The cross section of a titanium coating on a decarburized 0.36% C steel with tightly adhering scale prior to coating. 200x.
Conditions of decarburization: 950°C.; 2 hours
Coating Conditions:
Temperature: 950°C. Time: 8 hours
Bath composition: NaCl and Metallic titanium powder.
Furnace atmosphere: Air
Thickness = 0.1200 mm.

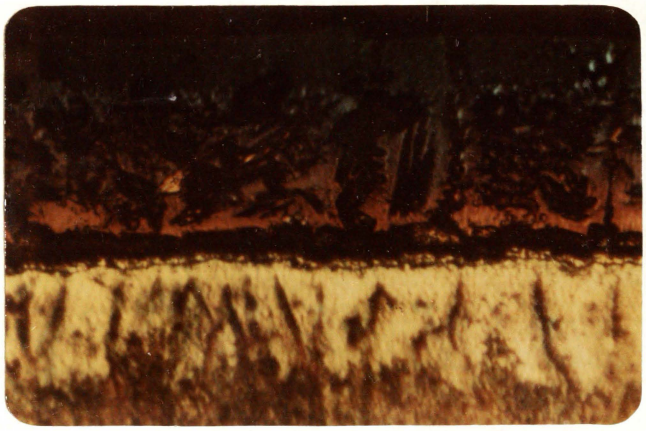


Fig. 26. The cross section of a titanium coating on ingot iron obtained by the iodide titanizing method. 200x.
Coating Conditions:
Temperature: 1000°C. Time: 4 hours
Bath composition: 10 gm iodine and 40 gm titanium fines.
Furnace atmosphere: Air
The coating appears in the upper portion of the photograph. The upper layer of the coating actually was a blue color, and the lower layer was reddish-violet in color. The diffusion layer appears in the lower portion of the photograph. Some voids are found between the coating and the diffusion layer.
Thickness in Coating = 0.1700 mm.

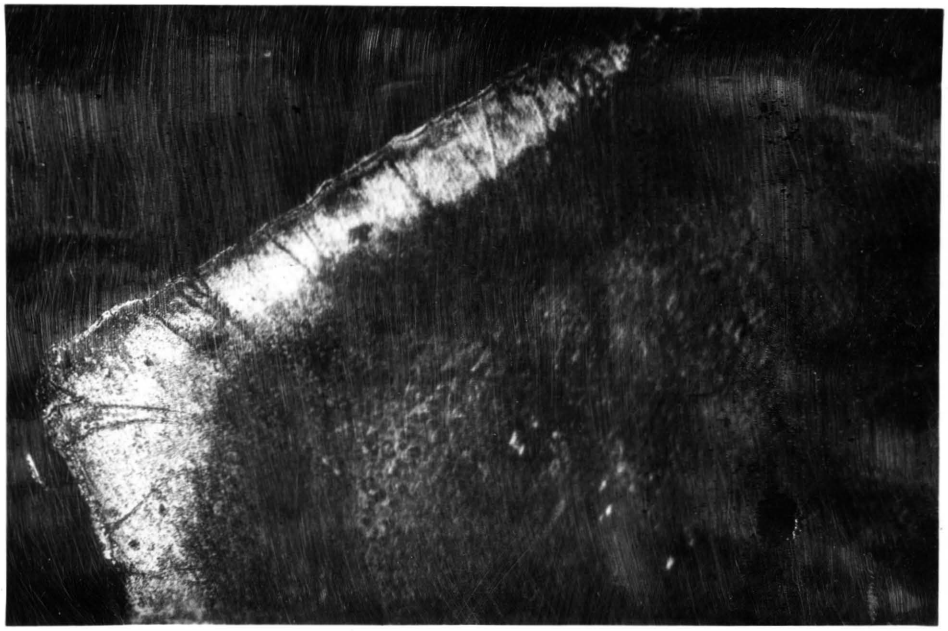


Fig. 27. The cross section of a titanium coating on ingot iron coated using the iodide titanizing method. 150x.
Coating Condtions:
Temperature: 1100°C. Time: 4 hours
Bath composition: 120 gm Al_2O_3, 120 gm Ti fines (+65 mesh), and 30 gm solid iodine.
Furnace atmosphere: Air
Thickness of Coating = 0.0129 mm.

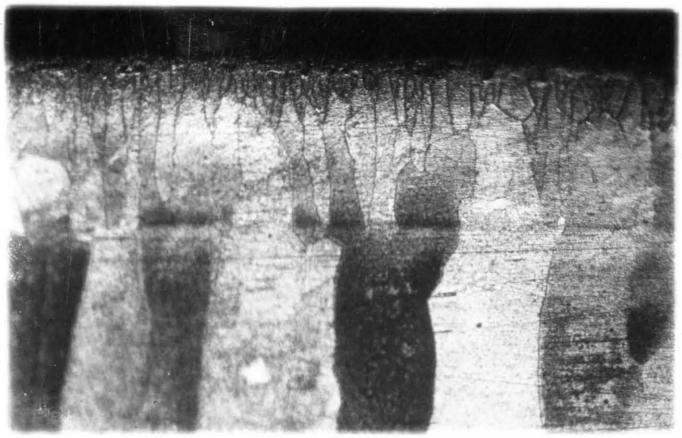


Fig. 28. The cross section of a titanium coating on ingot iron made by enclosing the base metal in a stainless steel wire cage, then coating by the iodide titanizing method. 100x.
Coating Conditions: Same as that shown under Figure 27.
Thickness of Coating: 0.0266 mm.

Fig. 29. The cross section of a titanium coating on ingot iron coated in the presence of ammonium chloride. 200x.
Coating Conditions:
Temperature: 1100°C. Time: 4 hours
Bath composition: 120 gm Al_2O_3, 120 gm Ti fines (+65 mesh), and 45 gm NH_4Cl
Furnace atmosphere: Air
(The base metal was enclosed in a stainless steel wire cage, then embedded in the bath for coating.
Thickness of coating=0.0133 mm.

Fig. 30. The cross section of titanium coating on 0,15% C steel coated in the presence of ammonium chloride. 150x.
Coating Conditions:
Temperature: 1100°C Time: 4 hours
Bath composition: 120 gm Al_2O_3, 120 gm Ti powder (+65 mesh), and 45 gm NH_4Cl
Furnace atmosphere: Air
(The base metal was enclosed in a stainless steel wire cage, then embedded in the bath for coating.
Thickness of Coating = 0.0101 mm.

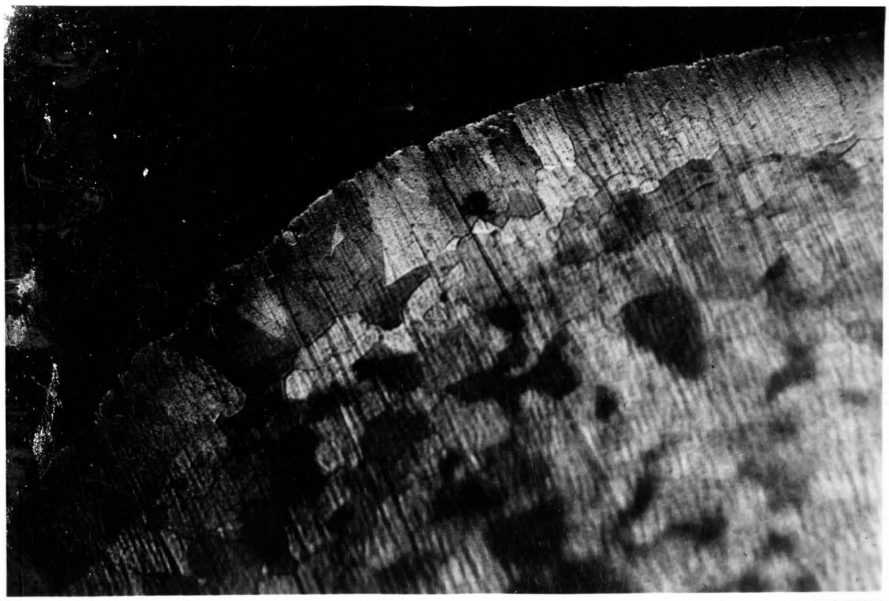


Fig. 31. The cross section of a titanium coating on ingot iron deposited in a titanium lower chloride. 250x. The sample was coated at 1100°C. for 4 hours. The coating is the fine white line along the edge of the sample.
Thickness of Coating = 0.0020 mm.

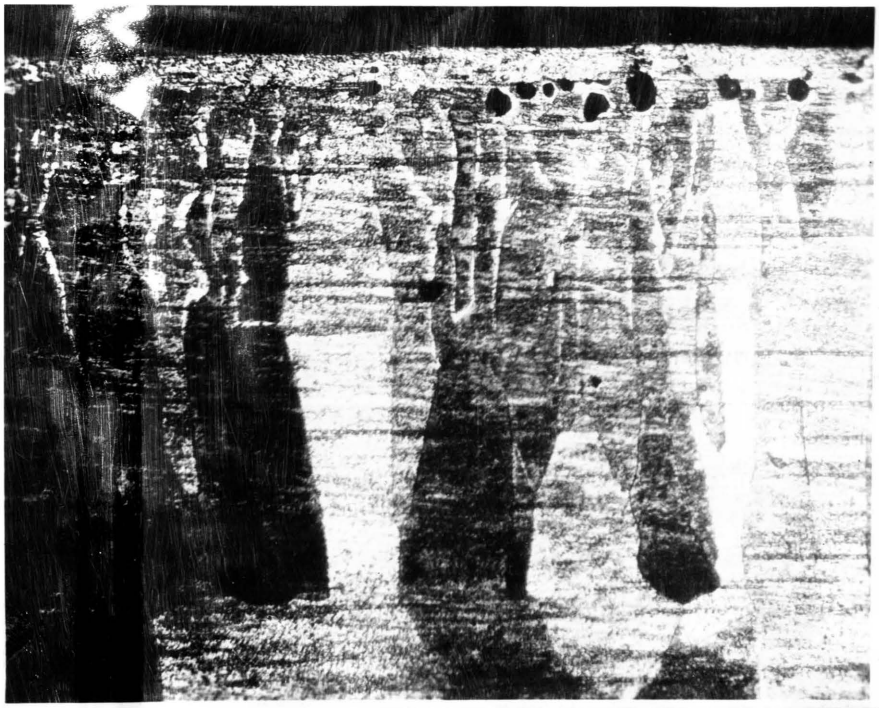


Fig. 32. The cross section of a titanium coating on ingot iron obtained in the presence of hydrogen chloride gas. 150x. The coating was made by passing dey hydrogen chloride gas through heated (at 1100°C. for 3 hours) titanium powder in which the base metal was embedded. Thickness of Coating = 0.0250 mm.

Fig. 33. The cross section of a titanium coating on ingot iron obtained in the presence of hydrogen chloride gas. 150x.
This is a corner of the same sample as the one shown in Figure 32.

DISCUSSION AND CONCLUSION

A. Theoretical Background for Interpretation of Data.

According to Rhines[1], the diffusion process will affect important changes in the physical characteristics of the bodies involved when relatively broad ranges of solid solubility or of compounds, or of both exist in a corresponding system. As reported by Vogel and Erang[12], the solubility of titanium in alpha iron reaches a maximum at about 6.9 percent at a temperature of 1300°C. (2370°F.), but decreases to perhaps 2 percent or less at room temperature. Tofaute and Buttinghaus[13] found the solubility as 6.3 percent at about 1350°C. (2460°F.), and as about 2.8 percent at 700°C. (1290°F.). Titanium combines with iron to form intermetallic compounds of FeTi identified by Witte and Wallbaum[14]. Wallbaum[15] also suggested the existence of $FeTi_2$ and indicated that the high titanium part of the system is solid at least up to 1550°C. (2732°F.). Titanium is also a carbide forming element, and the existence of TiC was reported by Hawkes[7]. Viewing the afore mentioned behavior of titanium, it is probable that the titanium diffusion coating on iron and steel will affect important changes in the characteristics of there base metals.

---

(12) Vogel, R., and Erang, R., Das System Eisen-Eiser wofram id-Eisen titanid, Archi f. d. Eisenhuttenwesen, Vol. 12, 1938, pp. 1 9-153.

(13) Tofaute, W., and Buttinghaus, Die Eseneke des system Eisen-Titan-Kohlenstoff, Archiv f. d. Eisen huttenwesen, Vol. 12, 1938, pp. 33-37.

(14) Witte, H., and Wallbaum, H. J., Thermische und rontegenographische untersuchung in system Eisen-Titan, Z. f. Metallukunde, Vol. 30, 1938, pp. 100-102.

(15) Wallbaum, H. J., Arch Eisenhuttenw, Vol. 12, 1941, p. 521.

If diffusion occurs at a substantially constant temperature and pressure, the layers form in kind and in the order of their occurrence to all regions in the phase diagram. These regions lie between the concentrations of the original bodies, and have three or more degrees of freedom according to the phase rule. In the conventional temperature-concentration section where pressure is disregarded, the degrees of freedom are two or three. The relative thickness of the various layers is determined by the breadth of each corresponding homogeneity range and by the rate of diffusion in each range. A relatively broad solubility range and a relatively high rate of diffusion should produce a relatively thick layer in the diffusion sample. The rate of diffusion increases in an alloy series as the melting point approaches the diffusion temperature(1).

In this investigation, the coatings studied deal with ternary or even more complicated systems. For instance, in the case of titanium coating on ingot iron coated in a fused salt bath containing a titanium-oxygen alloy, the constituents were titanium, oxygen, and iron, in the case of the same titanium coating on steel, the constituents were titanium, oxygen, iron, and carbon; and in the case of the bath in which silicon or zirconium, the number of constituents was even more than those of the former cases. Unfortunately the mechanism of diffusion in such processes is not yet clear and the constitutional diagrams concerning these systems are not well established. Therefore the identification of phases in these coatings is impossible at present.

---

(1) Rhines, F. N., op. cit. pp. 123-124.

When the diffusion process results in the formation of a diffusion layer which is often accompanied by recrystallization and grain growth, this layer is usually composed of columnar crystals with their long axes lying parallel to the direction of growth. Preferential diffusion usually takes place along grain boundaries and in a certain crystallographic direction. Exceptions to this common behavior are found chiefly when two or more phases occur together in the new layer, as in ternary systems or where precipitation occurs on cooling(1). Examples of the columnar recrystallization phenomenon in various samples as shown in Figures 12, 13, 14, 21, 27, 28, 29, 31, and 33.

In these samples, titanium probably together with oxygen diffused into the base metal to a considerable depth which varied with the temperature and with the length of coating time. Exceptions to this common behavior were also found in those samples as shown in Figures 15, 16, 17, 20, 23, and 30. As these coatings were made on plain carbon steels, there were at least three constituents in each case, namely: titanium, iron, and carbon, and the carbon contents in those steels were high enough to form titanium carbide, which precipitated and blocked the inward diffusion of titanium. Voids were sometimes found in one or more layers of titanium diffusion coatings of many samples. No proper explanations could be given, nor were any available in the literature.

The samples shown in Figure 13 was coated under helium atmosphere by heating an ingot iron plate in a mixture consisting of about 90 percent potassium chloride, 10 percent titanium oxygen alloy

---

(1) Rhines, F. N., op. cit. p. 134.

containing 5 atomic percent oxygen, with a small amount of silicon powder. It had a diffusion zone composed of elongated crystals with broad grain boundaries. According to Sauveur[16], silicon combines with iron to form the compound FeSi, which in turn forms solid solutions both with gamma and with alpha iron. The structure of the diffusion layer of this sample shown in Figure 13 resulted probably from the solution of silicon iron. Another sample shown in Figure 14 was coated under the same conditions without silicon in the bath. The structure of the diffusion layer of this sample was quite different from that of the sample shown in Figure 13.

The addition of silicon to the coating bath helps the growth of a titanium diffusion coating in carbon steel. Figure 15 shows the titanium coating on 0.36% carbon steel made at 1050°C. for 3 hours in a bath containing 90 percent potassi chloride and 10 percent titanium fines. The coating was very thin (0.004 mm.) and no diffusion layer could be detected. Figure 16 shows the coating on the same steel made at similar conditions except that a small amount of silicon powder was added to the bath. This coating was almost twice as thick as that shown in Figure 15. According to Minkevich, the diffusing silicon retards the accumulation of carbon as it causes the carbon to diffuse inward toward the core of steel.

---

(16) Sauveur, A., The Metallography and Heat Treatment of Iron and Steel, McGraw-Hill Book Co., 1946, p. 360.

(17) Minkevich, A. N., Translated from author, Surface Impregnation of Steel With Nickel, Cobalt, Titanium, Zirconium, Tantalum, and Manganese. Chapter XIV Published by Mashgiz, Moscow, 1950.

Figures 22, 23, and 24 show the cross section of titanium coatings 0.12, .15, and 0.36 percent carbon steels respectively. The thickne ses of coatings of these samples decreased with increase of carbon content of steel, from 0.0120 mm. with 0.12% C steel to 0.0030 mm. with 0.36% C steel. A good titanium coating was not obtained on steel containing 0.36 percent. However, with addition of vanadium oxydichloride to the salt bath, the o.36 percent carbon steel could be very well coated. (Figure 24.) Vanadium oxydichloride decomposes at high temperature and th vanadium metal formed dissolves in steel acting as a very strong carbide. The formation of vanadium carbide up the carbon in the steel sample and promotes the diffusion of titanium.

Decarburization reduces the carbon concentration of the surface layer. If decarburization is carried out at temperatures from 730 to 895°C. (1350 to 1640°F.), the formation of ferrite will take place.(18) Such a decarburized steel has a ferrite layer on its surface of so low a carbon content, that the formation of titanium carbide does not occur. Therefore decarburization helps the diffusion of titanium. Figure 25 shows the titanium coating on a decarburized steel.

Thick coatings exhibit a strong tendency to crack especially at sharp corners as shown in Figure 25 and 26. During the coating process, the grain growth of the base metal occurred at the inside

---

(18) Pennington, W. A., A Mechanism of The Surface Decarburization of Steel, Trans. American Society of Metals, Vol. 37, p. 48, 1946.

of the coating, which probably increased in dimension and therefore cracks were developed on the titanium nitride layer.

Figure 27 shows a sample obtained by heating ingot iron at 1100°C. for 4 hours in a bath consisting of 120 grams alumina, 120 grams titanium powder (+65 mesh), and 30 grams iodine crystal. During the coating process the iodine probably acted as a carrier substance which reacted with titanium powder to form titanium iodide which was subsequently decomposed at the surface of the sample depositing metallic titanium on it. As some titanium powder was in direct contact with the object the former diffused into it. Because of the non-uniform distribution of titanium powder in the mixture, the coating produced became quite uneven.

Figure 28 shows another sample made by enclosing the base metal in a stainless steel wire cage which was then embedded in the same mixture and was heated at the same temperature for the same time as used for the sample mentioned last. The even coating on this sample was titanium produced by the decomposition of titanium iodide with titanium deposited at the surface of the base metal.

Figure 32 shows the cross section of a sample which was prepared by passing dry hydrogen chloride gas through heated titanium powder (at 1100°C. for 3 hours) in which an iron specimen was embedded. The cavities in the diffusion zone probably resulted from the corrosion of ingot iron by hydrogen chloride, because much $FeCl_2$ was found in the glass tubing of the experimental arrangement.

B. Experimental Difficulties and Sources of Errors

Successful metallographic examinations of titanium metal and titanium diffusion coatings on ingot iron and plain carbon steels require that the final polish on the prepared surface be of high order and that the method of preparation yield a surface which is which is intrinsically characteristic of the sample itself. The electrolytic polishing alleviates many of the difficulties encountered in mechanical polishing, but it also introduces some disadvantages, such as staining of samples mounted in lucite, chemical attack of the lucite by electrolyte, formation of an undulated polished surface rather than one that is plane.

The important factor contributing towards successful electrolytic polishing is the relationship established between current density and voltage for a given electrolyte and electrolytic current arrangement, especially of the perchloric acid type electrolytes. The current-voltage data for electrolytic polishing is entirely absent. When the voltage exceeded the limiting voltage for successful polishing, sufficient gassing occurred at the sample surface to break down the continuously covering boundary layer as fast as it was formed. So the condition for successful electrolytic polishing is not easy to attain.

Mechanical polishing for cross sections of samples often causes the coating to be partially peeled off or deformed, and rounding at the edges occurs. It is almost impossible to reduce these defects.

The colors developed on different constituents of titanium coatings and diffusion layers largely depend upon the time of etching. The cycle of etching should be kept accurate within a fraction of a second, which is also difficult to achieve.

A color photomicrograph can reproduce very closely the colors of the constituents developed by cumulative electrolytic s ain-etching, but the color prints, (ordered from Washington Color Photo, Washington D. C.) made out from these photographs do not reproduce the original colors.

The following errors were introduced in the measurement of thickness of titanium diffusion coatings: (1) the sample could not always be put exactly in a vertical position, (2) personal errors in the reading of decimal digits of the eyepiece micrometer scale.

C. Conclusion

The cumulative electrolytic stain etching technique furnishes a good method for the examination of titanium diffusion coatings on iron and steel. Although the ordinary chemical etching method can be used to distinguish the coating, the diffusion layer, and the base metal core from one another and to reveal their structures, yet it cannot differentiate the composite layers within the coating when the latter consists of more than one layer.

By cumulative electrolytic stain etching, one can readily see the different layers within the coating in different shades of colors. The diffusion layer and the core metal also slow up in different colors by the stain etching method. The development of color by stain etching facilitates identifying these layers under the microscope and offers a remarkable advantage over the ordinary chemical etching method.

For identification of the phases present in the titanium diffusion coatings, the constitutional diagrams of alloys containing titanium and other elements present in the coating must be consulted(1). The titanium diffusion coatings on ingot iron or mild steels made in the fused alkali chloride baths probably contain a few percent of oxygen, in addition to titanium and iron(19).

---

(1) Rhines, F. N., op. cit., p. 123

(19) Schlechten, A. W., Straumanis, M. E., and Gill, C. B., Deposition of Titanium Coatings from Pyrosols, J. Electroch. Soc. Vol. 102, 1955, p. 81.

Coatings made by other methods (such as by the use of iodine or ammonium chloride) may also introduce other elements into the coating. These variables make the identification of the phases very difficult ecause very little is known at present time about the ternary alloys systems such as titanium-iron-oxygen, titanium-iron-nitrogen, etc. The presence of carbon in steels further complicates such studies. Because of the lack of available data concerning the more complicated alloy systems of titanium, definite conclusions can not be reached yet as to the identification of the various phases present in the titanium diffusion coatings observed under the microscope in this investigation. Undoubtedly the outermost layer of coating must be alpha-titanium, containing some iron in solid solution. Beyond this point nothing can be said very definitely.

It is hoped that future studies of titanium alloy systems such as titanium-iron-oxygen, titanium-iron-nitrogen, etc. will help clear this problem.

SUMMARY

For the metallographic examination of the structure of titanium coatings on metals especially on mild steels, the respective samples were polished by mechanical means and samples of titanium metal were electrolytically polished. A diamond compound was used as an abrasive in the final stage of mechanical polishing to give scratchfree surfaces. The well polished samples were then etched with an aqueous etchant, containing hydrofluoric acid and nitric acid. The structure of titanium metal and titanium diffusion coatings were revealed after etching.

Cumulative electrolytic stain etching method, based on a differential rate of oxidation of microconstituents, was found very satisfactory to differentiate the coating from the diffusion layer and the core metal. Various colors were developed by different layers of the titanium coating and by the diffusion zone.

In steels containing more than 0.15 percent carbon, the precipitation of titanium carbide blocked the diffusion of titanium into the core metal. Decarburization of steel and the addition of silicon, zirconium, or vanadium oxydichloride ($VOCl_2$) to the bath was promoted deposition process.

The titanium coatings on ingot iron made at 850°C did not show diffusion layers. The diffusion layers observed on samples

obtained at temperatures above 900°C were composed of columnar crystals with their long axes lying parallel to the direction of growth.

The thicknesses of titanium coatings were measured under a microscope using a calibrated screw eyepiece micrometer.

The thicknesses of coatings and of diffusion layers of ingot iron samples coated in fused chloride baths containing titanium-oxygen alloys were found to increase with the coating temperature, coating time, the titanium content of the titanium-oxygen alloy used, and the concentration of the alloy in the bath.

The iodide titanizing method produced thick coatings (0.1700 mm.) on ingot iron, but in such coating cracks were often found. The titanium coatings on ingot iron and 0.15 percent carbon steel made in the presence of ammonium chloride, and the titanium coatings on ingot iron made in the presence of hydrogen chloride gas were thick and even, but in the latter case the base metal was corroded very seriously.

Almost all the titanium diffusion coatings studied in this inves igation dealt with ternary or more complicated systems. For lack of well established constitutional diagrams of the system concerned, it is not yet possible to identify the various phases present in the coating.

BIBLIOGRAPHY

Abendroth, R. P., Effect Of Carbon Content In Steels Upon The Deposition Of Titanium From A Fused Salt Bath, M. S. Thesis in Metallurgy, Missouri School of Mines and Metallurgy, 1954, pp. 9-10.

Comstock, G. F., Urban, S. F., and Cohen, M., Titanium in Steel, Pitman Publishing Corporation, 1949, p. 48.

Dovey, D. M., Jenkins, I., and Randle, K. C., Diffusion Coatings, Properties of Metallic Surfaces, Inst. of Metals Monograph, No. 13, 1952, pp. 213-236.

Ence, E., and Magolin, M., Phases in Titanium Alloys Identified by Cumulativ Etching, J. of Metals, Vol. 6, No. 3, March, 1954, pp. 346-348.

Hadley, R. L., and Derge, G., Equilibrium Between Titanium in Liquid Iron and Titanium Oxides, J. of Metals, Vol. 7, Jun., 1955, Sec. 1, pp. 55-60.

Hawkes, M. F., Constitutional Diagram of Carbon-Iron-Titanium, Metals Handbook, American Society for Metals, 1948, p. 1225.

Jaffee, R. I., General Physical Metallurgy of Titanium Reviewed, J. of Metals, Feb., 1955, Sec. 1, pp. 247-252.

Minkevich, A. N., Translated from author's book, Surface Impregnation of Steel With Nickel, Cobalt, Titanium, Zirconium, Tantalum, and Manganese. Chapter XIV, Published by Mashgiz, Moscow, 1950.

Pennington, W. A., Mechanism of The Surface Decarburization of Steel, Trans. American Society of Metals, Vol. 37, P. 48, 1946.

Rhines, F. N., Diffusion Coatings on Metals, A. S. M. Surface Treatment of Metals, 1949, p. 123-134.

Schlechton, A. W., Straumanis, M. E., and Gill, C. B., Deposition of Titanium Coatings from Pyrosols, J. Electroch. Soc. Vol. 102, 1955, p. 81.

Sauveur, A., The Metallography and Heat Treatment of Iron and Steel, McGraw-Hill Book Co., 1946, p. 360.

Shih, S. T., and Straumanis, M. E., Progress Report No. 12, July, 1954, Electrodeposition of Titanium Project, Contract No. AF 33(616)-75, U. S. A. F.

Shih, S. T., and Straumanis, M. E., Progress Report No. 11, Dec., 1964, Electrodeposition of Titainum Project, Contract No. AF 33(616)-75, U. S. A. F.

Tofaute, W., and Buttinghaus, Die Esenk des system Eisen-Titan-Kohlenstoff, Archiv.f. d. Eisem huttenwesen, Vol. 12, 1938, pp. 33-37.

Wallbaum, H. J., Arch Eisenhuttenw, Vol. 12, 1941, p. 521.

Witte, H., and Wallbaum, H. J., Thermische und röntgenographische Untersuchung im System Eisen-Titan, Z. f. Metallkunde, Vol. 30, 1938, pp. 100-102.

Worner, H. W., The Constitution of Titanium Rich Alloys of Iron and Titanium, J. of the Inst. of Metals, Vol. 79, May, 1951, pp. 173-188.

VITA

The author was born in Shanghai, China, on December 24, 1924. He attended the Dah Kwang Primary School at Shanghai, and graduated from the Kiangsu Provincial Youngchow Middle School, Kiangsu, China, in 1942. He attended the National Chungking University, China, in September 1943, and received a B. E. degree in Metallurgical Engineering in June 1947. He was awarded a Titanium Fellowship in the department of Metallurgical Engineering at the Missouri School of Mines and Metallurgy in September 1954 to work toward his M. S. degree in Metallurgical Engineering.